

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : <b>A23G 9/02, A23D 9/00</b>		<b>A1</b>	(11) International Publication Number: <b>WO 95/29596</b> (43) International Publication Date: <b>9 November 1995 (09.11.95)</b>
(21) International Application Number: <b>PCT/EP95/01572</b> (22) International Filing Date: <b>25 April 1995 (25.04.95)</b> (30) Priority Data: <b>94303170.8 29 April 1994 (29.04.94) EP</b> (34) Countries for which the regional or international application was filed: <b>AT et al.</b> (71) Applicant (for all designated States except US): <b>LODERS CROKLAAN B.V. [NL/NL]; Zaandijkeweg 36, NL-1521 AX Wormerveer (NL).</b> (72) Inventors; and (75) Inventors/Applicants (for US only): <b>CAIN, Frederick, William [GB/NL]; Drive Blookerstraat 12, NL-2271 VL Voorburg (NL). MANSON, Helga [GB/NL]; Colorado 4, NL-1186 HX Amstelveen (NL). QUINLAN, Paul, Thomas [GB/GB]; 9 Ely Way, Kempston, Bedford MK42 8TW (GB). MOORE, Stephen, Raymond [GB/GB]; 2 Wainwright Avenue, Thrapston, Northamptonshire NN14 4UH (GB).</b>		(81) Designated States: <b>AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).</b>  Published <i>With international search report.</i>	
(54) Title: <b>ICE-CREAM COATING FATS</b>			
(57) Abstract  Novel ice-cream coating fats based on diglycerides comprise at least 30 wt. %, preferably 50-90 wt. %, of diglycerides, which diglycerides have an SU content of 10-25 wt. %, while the total fat composition has a SAFA content of 5-35 wt. % and an N line (unstab.) of N <sub>20</sub> <35 and N <sub>25</sub> <10.			

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

ICE-CREAM COATING FATS

Ice-cream coating fats known so far are mainly based on triglycerides, in particular triglycerides containing  
5 medium-chain fatty acid residues, such as lauric acid residues. Typical examples of such fats are disclosed in, e.g., EP 23,150, US 5,017,392, US 4,560,563, US 4,086,370 and US 3,959,516. However, hydrogenated vegetable non-lauric fats and triglycerides high in polyunsaturated fatty  
10 acids are also known as ice-cream coating fats, e.g. from EP 502,697, EP 246,366, EP 23,151 and US 3,333,968.

Hitherto, no composition has been disclosed that is based on diglycerides and is suitable as ice-cream coating fat.

15 According to EP 402,090 oil-in-water emulsions are known, in which the fat phase comprises 10-99 wt.% of a diglyceride mixture having an increasing melting point of at most 20°C, which mixture can also contain some  
20 monoglycerides, the total glyceride blend having a melting point of 35°C or below. These emulsions are suitable as cream alternatives and for ice-cream application. For the latter application, however, the emulsion is used for the ice-cream mass and not for the coating of the ice cream.

25 We have studied how to develop ice-cream coating fats that have a low SAFA content (a maximum of 35 wt.%) and an N-line that renders them suitable as ice-cream coating fat and which fat composition would be based on the presence of  
30 a minimum amount of diglycerides. The above-mentioned study resulted in novel fat compositions being found that are suitable for ice-cream coatings. These novel fat compositions comprise at least 30 wt.%, preferably 50-90 wt.%, of diglycerides, which diglycerides have an SU  
35 content of 10-25 wt.% (S = saturated fatty acid residue; U = unsaturated fatty acid residue), while the fat composition displays a SAFA content of 5-35 wt.% and an N

line (NMR pulse, not stabilized) of  $N_{20} < 35$ , preferably 1.0-20, more preferably 1.0-5.0;  $N_{25} < 10$ , preferably  $< 1.0$ .

Although known ice-cream coating fats, such as coconut oil  
5 or cocoa butter, have an  $N_{20}$  of at least 40, it was found, unexpectedly, that fats with a lower  $N_{20}$  can also be applied as ice-cream coating fats; however, the fats should contain enough of the required diglycerides.

10 The above-mentioned finding therefore contradicts the general belief that a high  $N_{20}$  is a prerequisite for obtaining high crystallisation rates and acceptable drying times.

15 In particular, the diglyceride part of our novel fat compositions has a  $U_2$  content of 75-90 wt.% and an  $S_2$  content below 5 wt.%.

In a preferred embodiment of our invention the fats display  
20 an  $N_0$  of more than 35, in particular  $N_0 = 45-80$ . It was found that, when  $N_0 > 80$ , the coating became too brittle, while below  $N_0 = 35$  the coating was too soft. The  $N_{20}$  controls the oral mouthfeel (waxiness) and meltdown of our ice-cream coating compositions.

25 As coconut oil and cocoa butter have relatively high  $N_{20}$  values, whereas our fats have low  $N_{20}$  values, the oral meltdown of our fat compositions is much shorter than the meltdown of coconut oil- or cocoa butter-based fat  
30 compositions.

Our diglyceride compositions are based on diglycerides derived from fatty acid residues with 12-24 C atoms, preferably 16-22 C atoms (for the saturated fatty acid  
35 residues (S)), and for the unsaturated fatty acid residues (U) these acids have at least 16 C atoms, preferably 18 C atoms; in particular, U is oleic acid.

Diglycerides can exist as both the sn-1,2 (sn-2,3) and sn-1,3 isomers. Both isomers can be applied in the present invention. In a preferred embodiment of our invention, however, products enriched in the sn-1,3 isomer are applied. Preferably, a ratio of sn-1,3/sn-1,2 diglyceride isomers > 2.5 is applied to increase the melting profile of the blend. Diglyceride fractions enriched in the sn-1,3 isomer can be prepared by fractionation (in solvent or dry); solvent fractionation using hexane is preferred.

Our novel fat compositions can also contain some triglycerides. Preferred compositions also comprise 10-50 wt.% of a vegetable triglyceride composition, preferably having a total ( $U_3 + U_2S$ ) content of at least 50 wt.%.

Although our triglyceride compositions can be manufactured by blending of their components, either as pure components or as mixtures of components, a preferred way of producing our fats is by performing a glycerolysis of a liquid oil and glycerol. This glycerolysis can be performed by using an enzyme, preferably a 1,3-specific enzyme, or by using a base, such as sodium methanolate.

The reaction conditions for an enzymatic conversion of a liquid oil with glycerol are typically :

weight ratio oil : glycerol 1:10 to 100:1;

reaction times : 6-120 hours;

temperature : 0-40°C

enzymes : selected from *Rhizopus*, *Rhizomucor*,

*Pseudomonas*, *Candida*, and preferably

*Humicola*. The enzymes are used in amounts of 100-1000 LU/gm of oil.

The oils that can be applied for the above-mentioned conversion are typically : sunflower oil, high-oleic sunflower oil, safflower oil, high-oleic safflower oil, corn oil, cottonseed oil, rapeseed oil, olive oil and

soybean oil.

After separation from residual glycerol, the crude glycerolysis product is processed to produce the final  
5 product by evaporation to remove monoglycerides and optionally fractionation (dry or solvent). This can lead to an optimum ratio of diglycerides to triglycerides in the mixture and this post-treatment can be used to control the N values (in all instances NMR pulse measurements were  
10 performed on non-stabilised fats, i.e. after the fats had been stored at 0°C for 90 minutes) or the SAFA content of the product. Sometimes it can be suitable to subject the fats as obtained to a refining treatment (using bleaching earth and steam).

15

A typical ice-cream coating composition comprises the following formulation :

- 35-55 wt.% of a polysaccharide, preferably sugar;
- 20 25-65 wt.% of the fat composition according to the invention;
- 0-20 wt% of cocoa powder, preferably 5-15 wt.%;
- 0-10 wt.% of a milk component, preferably skim-milk powder;
- 25 0-2 wt.% of an emulsifier, preferably lecithin.

Part of our invention are also ice creams coated with the above-mentioned ice-cream coating compositions.

EXAMPLE 11.1 Glycerolysis of high-oleic sunflower oil

5 High-oleic sunflower oil (having the composition given below) was reacted with glycerol in a ratio of 5 parts of HOSF oil to 1 part of glycerol by weight, in the presence of *Humicola* lipase (1000 LU/gm of oil). The reaction time was 24 hours and the temperature was 40°C. After separation  
 10 from glycerol, monoglycerides were removed by evaporation at 240°C and 1 mbar pressure. The resulting product was fractionated in hexane at -10°C; the product obtained was refined by a treatment with bleaching earth and steaming at 190°C for 4 hours to give a diglyceride-rich fraction of  
 15 the following composition :

	<u>C<sub>16:0</sub></u>	<u>C<sub>18:0</sub></u>	<u>C<sub>18:1</sub></u>	<u>C<sub>18:2</sub></u>	<u>C<sub>20</sub></u>	<u>% SAFA</u>
Product (= Fat A)	3.9	5.7	86.2	1.5	2.6	12.2
HOSF (= Fat B)	4.0	4.7	84.3	4.9	2.1	10.8

20

1.2 Preparation of another diglyceride-product (= fat E)

Two diglyceride-rich fat products (an olein and a stearin) were prepared from the glycerolysis of HOSF, followed by  
 25 separation techniques:

- a) 100:20:0.5 by weight of HOSF, glycerol, Lipolase 100 L enzyme (ex-Nove Nordisk) respectively, were stirred at 40°C for 24 hours.
- 30 b) Excess glycerol was decanted off, and mono-glycerides/FFA were removed from the crude reaction product (22.1 wt% DG, 3.8 wt% MG) in a falling film evaporator (260°C, 0.3 mm Hg abs.).
- 35 c) After refining, the diglyceride rich product was fractionated from hexane (2:1 hexane oil to oil by

weight at  $-12^{\circ}\text{C}$ ), collecting the olein (16.9 wt% DG, yield 90 wt%) and the stearin (63 wt% DG, 7.8 wt% MG, yield 10 wt%).

- 5 d) The olein product had a composition of:  
16.9 wt% DG, 0.8 wt% MG  
DG part 0.0% SS type, 15.1% SU type, 84.8% UU type.
- e) The diglyceride content of the olein product was  
10 increased by a two-stage silica treatment:  
i) Diglycerides and monoglycerides were absorbed  
onto silica, using hexane as a solvent (in the  
proportion 2:1:1 hexane, oil, silica by weight). The  
silica complex was washed with hexane (2.6:1 hexane to  
15 oil by weight) and the wash discarded.  
ii) The silica complex was washed with 88 wt% hexane/  
12 wt% acetone (3:2:1 wash to oil by weight), and the  
diglyceride-rich wash collected. A diglyceride-rich  
fat was formed by evaporation of the hexane/acetone  
20 solvent.
- f) The diglyceride enriched olein had a composition of:  
51.5 wt% DG, 0.1 wt% MG,  
DG part 0.0% SS type, 16.5 % SU type, 83.5% UU type.  
25
- g) Excess monoglycerides were removed from the stearin  
product via a silica treatment with hexane/acetone (88  
wt% hexane, 12 wt% acetone) as the solvent (5:1:1.21  
solvent, oil, silica by weight) washed with 3 parts  
30 solvent to 1 part oil (by weight). The stearin product  
was recovered from the wash solvent by evaporation.
- h) The silica treated stearin had a composition of:  
69.6 wt% DG, 0.3 wt% MG  
35 DG part 0.6% SS type, 25.1% SU type, 74.4% UU type.

A diglyceride-rich fat blend was prepared by blending the

silica treated stearin and diglyceride enriched olein in the ratio 30:70 by weight. The blend was bleached and deodorised.

- 5 The refined blend contained: 55.5 wt DG, 0.1 wt% MG.  
The DG composition was 0.4 % SS, 21.1 % SU, 78.5 % UU.

The FAME profile of the total blend was (wt%):

14:0	16:0	16:1	18:0	18:1	18:2	18:3	20	22	24
0.0	4.0	0.1	4.5	84.9	4.6	0.0	0.6	1.1	0.2

- 10 giving a total SAFA level of 10.1 wt%.

The triglyceride part contained 20 wt% of SOO and 65.9 wt% of OOO.

- 15 1.3 The glyceride compositions of the refined fat A, of the starting oil (= Fat B), of a chemically made product (Fat C), of coconut oil (Fat D) and of the second enzymically made fat (= E) were as follows :

20	(Wt.%)	<u>Triglyceride</u>	<u>Diglyceride</u>	<u>Monoglyceride</u>
	Fat		(1,3 + 1,2)	
	A	14.2	80.3	5.5
	B	98.0	2.0	-
	C	-	98	2
25	D	98.0	2	-
	E	44.4	55.5	0.1

- The melting profile of the refined fat composition was measured. Fat C is a product that is made using a chemical  
30 conversion with a base; Fat D is coconut oil.

		<u>Temperature (°C)</u>		
	Solids	0	20	25
	Fat			
35	A	42.0	2.7	0.1
	B	4.1		
	C	63.5	18.8	10.7

D	89.0	37.6	0
E	34.4	0.2	0

## 2. Ice-cream coatings

2.1 Ice-cream coatings were prepared, using the following

5 recipe :

	<u>Recipe :</u>	<u>wt.%</u>
	sugar	42.7
	fat	38.1
	cocoa powder D-11-MC	12.5
10	SMP	6.2
	lecithin	0.5

The fats applied were : cocoa butter (= CB), coconut oil (CN) and the refined enzymic conversion product of Example 15 1.1 and 1.2.

2.2 Ice creams were dipped in a melt of the above-mentioned ice-cream coating compositions.

20 The following results were obtained :

	<u>Fat</u>	<u>Coating T</u> (°C)	<u>Dripping time</u> (sec)	<u>Drying time</u> (sec)	<u>wt.%</u> of coating
25	CB	40.5	17	122	36
	Enz. conv. product A	41.0	25	99	26
	CN	38.5	22	73	36
30	Enz. conv. product E	40	23	97	32

35 The oral properties of the products were similar (all good-tasting). However the products according to the invention resulted in coatings that were softer and less brittle, which had quicker and smoother meltdown than CB-based coatings.

CLAIMS

1. Fat composition suitable for ice-cream coatings comprising at least 30 wt.%, preferably 50-90 wt.%, of diglycerides, which diglycerides have an SU content of 10-25 wt.% (S = saturated fatty acid residue; U = unsaturated fatty acid residue), while the fat composition displays a SAFA content of 5-35 wt.% and an N line (NMR pulse, not stabilized) of  $N_{20} < 35$ , preferably  $N_{20} = 1.0-20$ , more preferably 1.0-5.0,  $N_{25} < 10$ , preferably  $< 1.0$ .
2. Fat composition according to Claim 1, wherein the diglyceride part has a  $U_2$  content of 75-90 wt.% and an  $S_2$  content below 5 wt.%.
3. Fat composition according to Claims 1-2, wherein the fat compositions displays an  $N_0 > 35$ , preferably 45-80.
4. Fat composition according to Claims 1-3, wherein S has 12-24 C atoms, preferably 16-22 C atoms, and U has at least 16 C atoms, preferably 18 C atoms.
5. Fat composition according to Claims 1-4, wherein the composition also comprises 10-50 wt.% of a vegetable triglyceride composition, preferably having a total ( $U_3 + SU_2$ ) content of at least 50 wt.%.
6. Ice-cream coating composition comprising :
  - 35-55 wt.% of a polysaccharide, preferably sugar;
  - 25-65 wt.% of the fat composition according to Claims 1-5;
  - 0-20 wt% of cocoa powder;
  - 0-10 wt.% of a milk component, preferably skim-milk powder;
  - 0-2 wt.% of an emulsifier, preferably lecithin.

7. Coated ice creams wherein the ice-cream coating consists of the ice-cream coating according to Claim 6.

# INTERNATIONAL SEARCH REPORT

Internati Application No  
PCT/EP 95/01572

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A23G9/02 A23D9/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A23G A23D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP-A-0 477 935 (KAO CORPORATION) 1 April 1992 see page 2 - page 4; claims 1,3 ---	1-4,6,7
Y	EP-A-0 402 090 (KAO CORPORATION) 12 December 1990 cited in the application see page 3, line 1-16; claims 1-3 see page 4, line 1-49 ---	1-4,6,7
Y	EP-A-0 023 151 (UNILEVER LTD) 28 January 1981 cited in the application see claims 1,4; example 2 ---	1-4,6,7
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search

8 August 1995

Date of mailing of the international search report

21. 08 95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. : (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Kanbier, D

# INTERNATIONAL SEARCH REPORT

Internat Application No  
PCT/EP 95/01572

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 017 no. 693 (C-1144) & JP,A,05 236919 (KAO CORP.) 17 September 1993, see abstract ----	1
A	EP-A-0 483 414 (UNILEVER NV) 6 May 1992 see claims 1-6 ----	1,3,6,7
A	US-A-4 379 176 (THE PILLSBURY COMPANY) 5 April 1983 see column 3; claim 1 -----	5,6

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat

Application No

PCT/EP 95/01572

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0477935	01-04-92	JP-A- 4135455 US-A- 5326581	08-05-92 05-07-94
EP-A-0402090	12-12-90	JP-A- 3008431 JP-A- 3089936 JP-A- 3091451 DE-D- 69003014 DE-T- 69003014 ES-T- 2043279 HK-A- 56494 US-A- 5160759	16-01-91 15-04-91 17-04-91 07-10-93 16-12-93 16-12-93 03-06-94 03-11-92
EP-A-0023151	28-01-81	AT-T- 6020 AU-B- 540544 AU-A- 6120980 AU-B- 540545 AU-A- 6121080 EP-A, B 0023152 WO-A- 8100189 WO-A- 8100190 GB-A, B 2068706 GB-A- 2066646 US-A- 4396633 US-A- 4394392 AT-T- 2378 AT-T- 2710 AU-B- 542017 AU-A- 6120680 EP-A, B 0023150 WO-A- 8100191 US-A- 4430350	15-02-84 22-11-84 13-02-81 22-11-84 13-02-81 28-01-81 05-02-81 05-02-81 19-08-81 15-07-81 02-08-83 19-07-83 15-02-83 15-03-83 31-01-85 13-02-81 28-01-81 05-02-81 07-02-84
EP-A-0483414	06-05-92	NONE	
US-A-4379176	05-04-83	NONE	